

THE IMPACT OF LIQUEFACTION SOLVENT COMPOSITION ON HYDROGEN UTILIZATION EFFICIENCY

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INTRODUCTION

Hydrogen utilization efficiency in coal liquefaction is important not only because of the direct cost of H_2 , but more particularly because of the cost of the high pressure equipment that is required to hydrogenate solvent and coal structures even in the presence of catalysts. The effects of solvent composition on H-utilization efficiency would most readily be obtained from batch autoclave studies, where solvent composition can most easily be treated as an independent variable. However, such data are scarce because the rate of coal conversion is often the primary, if not the only, observable addressed.

In previous mechanistic work directed at understanding the modes of bond scission available for relevant coal structures, we observed experimentally that the selectivity and efficiency with which donatable hydrogen is used to cleave aryl-alkyl linkages in coal surrogates is highly dependent on the degree of hydrogenation of the donor (1-3). The observed variations in efficiency were well reproduced by a mechanistic numerical model incorporating the various competing H-transfer processes (3). The basic trend elaborated by the model is that an increase in the level of polycyclic aromatic hydrocarbon in the solvent can increase the efficiency of H-utilization markedly, at a minor expense in H-transfer rate. Conversely, solvents which are very low in the fully aromatic PCAH component tend to transfer hydrogen faster, but do it less discriminately, such that a much smaller fraction of the hydrogen transferred goes to produce hydrogenolysis, and more goes to simple ring hydrogenation. At that time we proposed that this trend in efficiency could have substantial implications for actual coal liquefaction, but we had no obvious examples at hand to cleanly support this assertion. The recent results of Mochida and coworkers (4) provide a very clear illustration of the relevance of our earlier projections. This demonstration of relevance includes the premise on which these conclusions were based, namely that H-transfer-induced bond scission plays a substantial role in coal liquefaction. In this paper we discuss Mochida's results in light of our earlier findings, and elaborate on the interactive effects of the H-donor and acceptor components of liquefaction solvents.

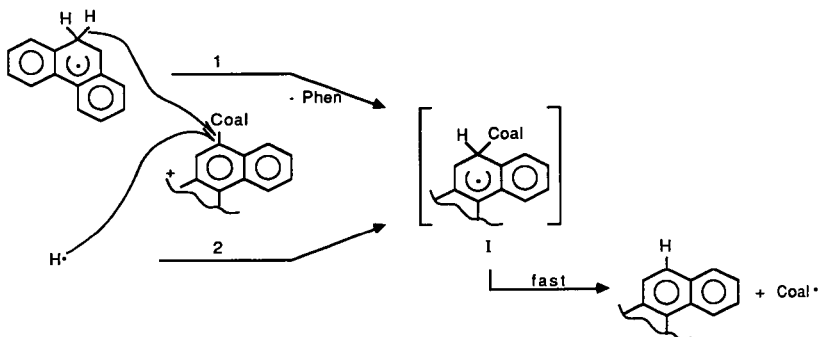
RESULTS AND DISCUSSION

Mochida et al. recently described the liquefaction of an Australian brown coal in tetrahydrofluoranthene (THFL), a donor solvent, containing varying amounts of fluoranthene (FL), a non donor (4). Their results show that although the conversion rates decrease as FL is added to the reaction mixture, the selectivity to oils (vs. gases) goes up somewhat, and the efficiency of H-utilization for oil production increases substantially. In Table 1 are shown the yields reported by Mochida for conversion in two media: 100% THFL and in a mixture of 75% THFL and 25% FL. In each case, the values shown are those reported at the time of maximum oil yield.

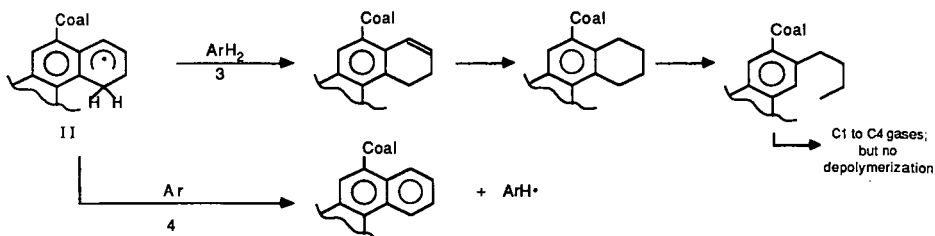
Replacement of 25% of the donor THFL with an equal amount of the non donor FL in the starting solvent increases the oil yield by five percentage points at the "expense"

of the gas yield. Substantially more pronounced is the impact of FL addition on the H-utilization efficiency (the ratio of oil produced to THFL consumed). As Table 1 shows, this value increases by 60%.

The origin of this change in efficiency cannot be understood without understanding the modes of H-transfer that lead to hydrogenolysis and/or hydrogenation. For this purpose, it is necessary to review some of our earlier findings. First, we can make the general statement that a shift in the utilization of hydroaromatic hydrogen could not occur without there being a shift in the mode of H-transfer. Specifically, if the addition of free H-atoms to positions on aromatic clusters bearing linkages (Reaction 1) were not in competition with the recently elucidated (1,2,5,6) radical hydrogen-transfer process (Reaction 2), there would be no basis for such a shift.



In Figure 1, we show previously presented (3) experimentally observed and numerically modeled H-utilization efficiency data for dinaphthylmethane cleavage. The reactions depicting the efficiency-determining competition in H-transfer processes are shown below:



It is not sufficient to consider merely the manner of formation of the ipso-substituted cyclohexadienyl radical I, because this intermediate, once formed at coal conversion temperatures, has an extremely short lifetime before elimination of virtually any linkage (as Coal•). In other words, cleavage will result no matter how I was formed.

Efficiency is determined by what happens to all of the radical species produced by H-transfer to positions not bearing linkages, II. When the concentration (and effectiveness) of polycyclic aromatic hydrocarbons that can act as hydrogen acceptors, transferring H-atoms back from non-ipso radicals, is low, then the non-ipso radicals are more likely to abstract a second hydrogen (e.g., from hydroaromatic in an "over hydrogenated" solvent). This dihydro intermediate is very reactive and will quickly be reduced to a tetrahydro intermediate. The tetrahydro intermediate can then receive additional hydrogens to open the aliphatic ring and crack off the 4-carbon chain as light hydrocarbons. In the example shown, this would mean that 6 or more hydrogens were consumed and no linkages were broken.

In contrast, when the concentration of H-acceptors is sufficient, the otherwise wastefully transferred hydrogen is recovered from the non-ipso radicals by the bimolecular RHT process, regenerating the hydrogen carrier radicals ArH^{\cdot} , so that the hydrogen transfer activity is maintained and there can be another chance at transfer to an ipso position. Ideally, this could result in having the only irreversible H-transfer being that to positions bearing linkages. In fact, the observed and computed hydrogen utilization efficiencies shown in Figure 1 indicate that, at least in the model system, a utilization efficiency approaching 90 to 100% can be achieved by merely adjusting the degree of hydrogenation.

When the original model compound studies were performed several years ago, we were surprised to observe that not only did the rate of hydroaromatic consumption go down when the solvent initially contained a significant amount of the respective aromatic, but that the absolute amount of hydroaromatic remaining at various reaction times could actually be larger when starting with less!

The final point to be recalled from our earlier studies is (as mentioned above) that the increase in H-utilization efficiency is achieved at some expense in terms of reaction rate. In the case of the data in Figure 1, when the efficiency showed a six-fold increase from 15% to 90%, the cleavage rate declined by about 60%. Closer examination of Mochida's data, as discussed below, shows that all of these trends are observed in the real coal liquefaction system.

Figure 2 shows the gas, oil, asphaltene, preasphaltene, and residue yields observed by Mochida as a function of time, when the starting solvent contained no fluoranthene, and when it contained 25% fluoranthene (4). In the 0% FL case, the oil yield develops faster, and the residue disappears more quickly, but in the 25% FL case, the more slowly developing oil yield reaches a 8% higher value at its maximum (which is at 30 min rather than 10 min), and the gas yield is only about 2/3 of that produced when the starting solvent is 100% THFL. This moderate advantage that results from starting with 25% FL becomes quite marked when the ratio of oil yield to THFL consumption is computed, revealing, as shown above in Table 1, a 60% increase in H-utilization efficiency.

The evolution of the solvent composition for these same two cases also shows the curious trend that there is equal or greater THFL remaining when the starting solvent contained less. For example, at 20 minutes the THFL concentration in the recovered solvent is 30% when starting with pure THFL and 35% when the starting with only 75% THFL. The extent of crossover is small and could easily be assigned it to experimental scatter, were it not for the fact that similar crossovers were also observed in our studies. The faster THFL decline is associated with a greater rate of production of perhydrofluoranthene. Thus in Mochida's case, as in our earlier model system studies, the absence of a significant initial concentration of PCAH allows multiple H-transfers and full reduction of some of the hydroaromatic species; one can infer that similar reduction without cleavage, followed by ring opening and gas production, are also occurring within the coal structures themselves.

A year ago, we presented a similar explanation (7) for excessive gas production when high temperature excursions occurred during coal hydropyrolysis as reported by Gorbaty and Maa (8). In this case the effectiveness of the PCAH systems as H-acceptors evidently decreased as a result of increasing temperature, thereby allowing greater ring reduction and ring opening. The chemistry we proposed was criticized as being excessively speculative. We find it gratifying to note that in the present case, careful analysis by Mochida of the recovered liquefaction solvents provides direct evidence for the anticipated wasteful reduction of aromatic systems.

Finally, we wish to suggest that the trend in H-utilization efficiency noted here is not merely a fortuitous result of scattered behavior. In an earlier publication, Mochida et al. described in less detail the liquefaction of three subbituminous coals in the fluoranthene solvent system (9). For two of the coals, a decrease in the starting THFL content from 100% to 67% resulted in an oils plus asphaltenes yield decrease of only 3%. Although THFL consumption was not detailed, given that the decreases in THFL consumption found in the more recent studies on brown coals were generally on the order of 40 to 45%, it can be presumed that in the case of subituminous coals too, the decrease in THFL consumption was much more than 3%. Thus, a trend in H-utilization efficiency similar to that observed for the brown coal probably also occurred for the subbituminous coals. Despite the fact that concern with conversion rate has tended to overshadow consideration of H-utilization efficiencies, other examples undoubtedly exist. For example, Derbyshire et al. earlier reported increased conversions in tetralin/pyrene mixtures as compared to pure tetralin (10). Although they did not report the consumptions of hydroaromatic, it once again is very likely that consumption decreased upon addition of pyrene. Similarly, more recent results of Cassidy et al (11) showing a substantial increase in absolute oil yields upon partial replacement of tetralin with pyrene probably also reflect increased H-utilization efficiency. Thus, we anticipate that a more thorough examination of the literature will provide many other examples.

We recognize that the apparent advantage of lower THFL concentration cannot be expected to transfer unchanged from the batch autoclave to continuous units. For example, the somewhat longer time required for disappearance of the THF-insoluble residue in the 75% THFL case (Figure 2b) could have a detrimental impact under large-scale continuous processing conditions, where persistence of an insoluble phase in the preheater could exacerbate coking on heat-transfer surfaces.

SUMMARY

The recent results of Mochida and coworkers, showing that modest decreases in conversion rate are accompanied by very substantial increases in hydroaromatic hydrogen utilization efficiency when 25% of the hydroaromatic in the starting solvent is replaced by the corresponding aromatic, provide significant confirmation of projections we had made earlier. These predictions were based on the premise that solvent-mediated hydrogenolysis of strong bonds plays an important role in coal liquefaction, and they required an understanding of the role of competitive H-transfer processes in these hydrogenolyses.

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Table 1

EFFECT OF REPLACEMENT OF PART OF TETRAHYDROFLUORANTHENE (H-DONOR) BY FLUORANTHENE (NON-DONOR) ON EFFICIENCY OF H-UTILIZATION AND SELECTIVITY TO OILS

THFL Content	PRODUCT YIELD*	
	100%	75%
Gas	18	13
Oil	63	68
Asph.	13	14
PA + Res.	6	5
Oil Yield		
THFL Consumption	1.1	1.7

* Optimal yield for coal conversion at
450°C/N₂/Solvent:Coal 3:1

Data from Mochida, 1988

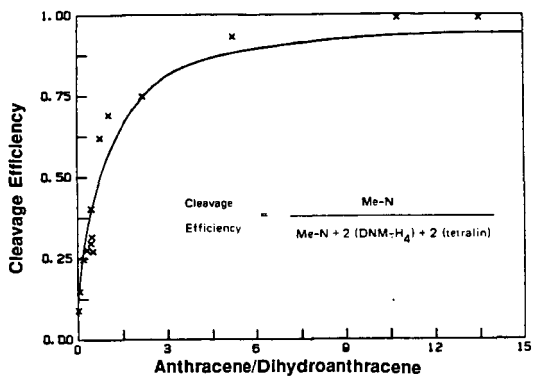


Figure 1. Experimental and Computed cleavage efficiency as a function of aromatic/hydroaromatic ratio

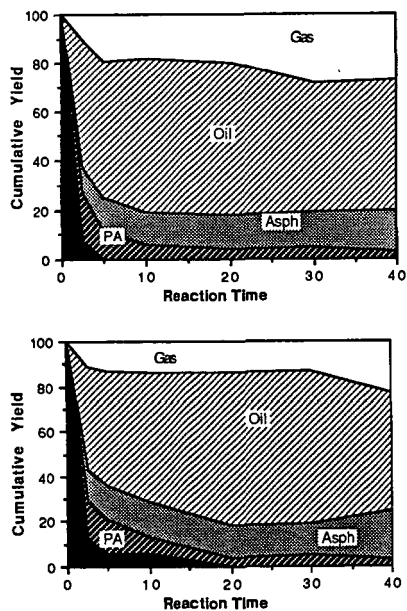


Figure 2. Product yields from conversion of an Australian Brown Coal in (a) 100% tetrahydrofluoranthene, and (b) a 75/25 mixture of tetrahydrofluoranthene and fluoranthene.

Data from Mochida, 1988